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Improvement in the luminescence efficiency of GaAsN alloys by photoexcitation

H. Yaguchi[*, 1], **T. Morioke**[1], **T. Aoki**[1], **Y. Hijikata**[1], **S. Yoshida**[1], **H. Akiyama**[2], **N. Usami**[3], **D. Aoki**[4], and **K. Onabe**[4]

[1] Department of Electrical and Electronic Systems, Saitama University, 255 Shimo-Okubo, Sakura-ku, Saitama 338-8570, Japan
[2] Institute for Solid State Physics, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581, Japan
[3] Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan
[4] Department of Applied Physics, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

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We found that photoexcitation with high excitation power density at low temperatures improves the luminescence efficiency of GaAsN alloys. From the temporal change of the PL intensity, the improvement occurs in a few minutes. Micro Raman study shows that structural changes occur in the laser-irradiated region. These indicate that the improvement of luminescence properties is due to photoexcitation-induced local structural changes. Since no distinct PL peak shift was observed after the laser irradiation at low temperatures, photoexcitation is a useful technique to improve the luminescence efficiency only.

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1 Introduction III–V–N alloys have been expected to be promising materials for optoelectronic device applications because of their unique properties [1–3], such as a huge band gap bowing, isoelectronic traps, and so on. In particular, (In)GaAsN is expected as a material for long-wavelength laser diodes with superior characteristic used in the optical fiber communications. Owing to its extreme immiscibility, however, it is necessary to lower the growth temperature for incorporating nitrogen atoms, and the luminescence efficiency is not always so high. Thus, thermal annealing after the growth is often carried out for improving luminescence properties of InGaAsN [4, 5]. In the present study, we report on the novel phenomenon that photoexcitation at low temperatures improves the luminescence efficiency of GaAsN alloys. This finding means that pure electronic excitation without thermal processes can improve the luminescence efficiency of GaAsN, i.e., the alloy system without In atoms, which are often attributed to the origin of the improvement or blue-shift in luminescence [4, 6]. In this paper, we also discuss photoexication-induced structural changes investigated by Raman scattering spectroscopy.

2 Experimental The samples used in this study were GaAsN alloys grown on GaAs (001) substrates by low-pressure metalorganic vapor phase epitaxy [7]. Trimethylgallium, arsine and 1,1-dimethylhydrazine were used as the Ga, As and N sources, respectively. The nitrogen concentration in GaAsN alloys was determined using X-ray diffraction. Micro photoluminescence (PL) measurements were permormed using a He–Ne laser (632.8 nm) focused to ~1.3 μm in diameter as the excitation source at 5 K. PL spectra were measured with first increasing and next decreasing excitation power density to clarify the photoexcitation effect on the improvement in the luminescence efficiency of GaAsN alloys. The

[*] Corresponding author: e-mail: yaguchi@opt.ees.saitama-u.ac.jp, Phone: +81 48 858 3841, Fax: +81 48 858 3841

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excitation power density was changed from 10–10^4 W/cm^2. The luminescence was detected with a 30-cm monochromator and an intensified charge coupled device camera.

3 Results and discussion Figure 1 shows the excitation power density dependence of PL spectra of $GaAs_{1-x}N_x$ ($x = 0.97\%$). Dashed and solid curves correspond to the spectra measured with increasing and decreasing excitation power density, respectively. After the photoexcitation with high power density at a low temperature, as can be seen from this figure, the PL intensities increase approximately 10 times even on the same excitation conditions, This clearly shows that the photoexcitation improves the luminesce efficiency of GaAsN and that the improvement is due to the pure electronic excitation without thermal processes.

Figure 2 shows the excitation power density dependence of the PL intensity of GaAsN. With increasing excitation power density up to ~1 kW/cm^2, the PL intensity almost linearly increases. When the sample is photo-excited with power densities >1 kW/cm^2, it is observed that the PL intensity begins to increase and is saturated in a few minutes. Such a threshold excitation power density for the improvement implies that considerable electronic excitation is necessary for breaking interatomic bonds and reconstructing local atomic configuration leading to the improvement in the luminescence efficiency, which will be described later. We confirmed that the luminescence efficiency was improved for GaAsN alloys with relatively high N concentrations ($x > 0.5\%$) and can be also improved by 532-nm laser irradiation with high power density. Remarkable improvement is observed for GaAsN alloys with high N concentration ($x > 0.5\%$) because more nonradiative recombination centers or deep levels due to structural defects are formed with N incorporation. Conversely, photoexcitation is not so effective in improving the luminescence efficiency of the samples with little structural defects. In addition, the improvement in the luminescence efficiency of GaAsN alloys is found to remain at higher temperatures and to be an irreversible process.

Figure 3 shows the temporal change of PL integrated intensity by photoexcitation with a power density of 10 kW/cm^2. The solid curve shown in this figure was obtained from fit to the experimental data using the following expression:

$$I(t) = I(0) \exp(-t/\tau) + I(\infty) \{1 - \exp(-t/\tau)\}. \quad (1)$$

This fit can explain well the temporal change of the PL intensity and the time constant is estimated to be 81 s. Since the improvement occurs in a time scale of a few minutes at a low temperature, this phenomenon is hardly related to the effect of inter-diffusion of atoms, which is often discussed in connection with the PL peak shift [4].

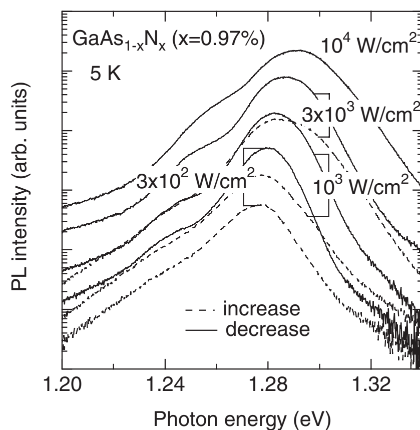

Fig. 1 Excitation power density dependence of PL spectra of GaAsN.

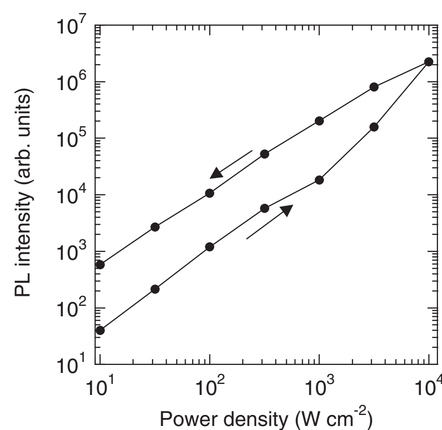

Fig. 2 Excitation power density dependence of the PL intensity of GaAsN.

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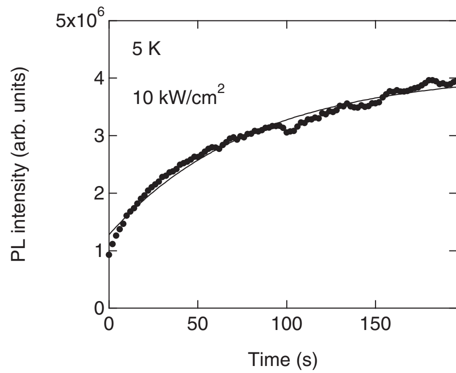

Fig. 3 Temporal change of the PL integrated intensity by photoexcitation.

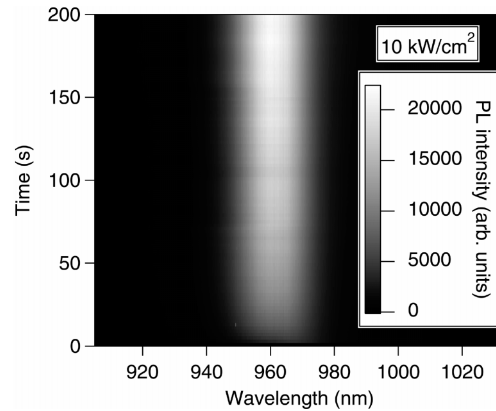

Fig. 4 Temporal change of the PL spectrum by photoexcitation.

Temporal change of PL spectrum by photoexcitation with a power density of 10 kW/cm^2 is shown as a 2D map in Fig. 4. As can be seen from this figure, no distinct PL peak shift was observed. This is different from the improvement in the luminescence efficiency by post-growth annealing, which leads to the PL peak shift to shorter wavelengths [4, 5]. Furthermore, high temperature annealing often causes the degradation of the crystal quality, and thus has the opposite effect of lowering the luminescence efficiency [4, 5]. In this light, photoexcitation is a useful technique to improve the luminescence efficiency only.

It is pointed out that the improvement of optical properties is related to structural changes [5, 6]. Therefore, we have used micro Raman spectroscopy to examine the structural changes due to photoexcitation. In the Raman spectrum in the vicinity of the laser-irradiated region, TO phonon peak, which is supposed to be forbidden in the backscattering measurement geometry, was more clearly observed. This suggests that some sort of photo-induced structural changes which lower crystal symmetry occur near the laser-irradiated region. Since this phenomenon is in a time scale of a few minutes, the photo-induced structural changes correspond not to long range inter-diffusion but local changes in atomic configuration, such as changes in the distance between atoms, annihilation of structural defects, or involvement of H atoms, which are related to the decrease in the density of nonradiative recombination centers or deep levels. It should be emphasized that the alloy system used in this study was GaAsN without In atoms. This unequivocally shows that the improvement in the luminescence efficiency observed in this study is completely unrelated to In atoms in contradiction to the previous study [6].

4 Conclusions We found that the luminescence efficiency of GaAsN alloys is improved by laser irradiation with high excitation power density at low temperatures. This improvement occurs in a few minutes and is related to local structural changes found from the result of micro Raman spectroscopy. Since the alloy system used in this study was GaAsN without In atoms, the improvement observed in this study is found to be completely unrelated to In atoms. In addition, no distinct PL peak shift was observed after the laser irradiation at low temperatures, which demonstrates that photoexcitation is a useful technique to improve the luminescence efficiency only.

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